

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Sheets of Polybutene-1

- We, PRINCETON CHEMICAL RESEARCH INC., a corporation organised and existing under the laws of New Jersey, United States of America, of Post Office Box 652, Princeton, New Jersey, United States of America, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—
- This invention relates to printing on polymers which are substantially opaque and which, on being subjected to total or selective pressure and/or heat, become transparent. Additionally, this invention relates to processes for opacifying such polymers. More specifically, this invention relates both to methods of manufacturing sheets or films of polybutene-1 which are substantially opaque and methods of subjecting opaque polybutene-1 to pressure or heat, whereby the polymer becomes substantially transparent in the areas treated.
- In the past, most printing operations have been conducted by physically transferring ink from a printing surface to a substrate and/or embossing or by selectively developing chemically treated substrates by chemical and/or physical means.
- It is an object of this invention to provide a non-embossing printing method that is a substantial departure from prior printing methods, and which represents an advance in the state of the printing art, whereby printing on a surface may be achieved without ink transference or by chemical means.
- Another object of the invention is to provide means for printing without substantial physical deformation of the print-receiving means.
- An additional object of this invention is
- to provide polybutene-1 polymers as film or sheets that are essentially opaque and will become substantially transparent upon being subjected to pressure and/or heat.
- The invention is based on the discovery that transparent to translucent film or sheeting, formed from substantially isotactic polybutene-1, may be stretched to provide a white, nearly opaque sheet or film. Subsequent selective or total application of pressure and/or heat to the surface of the sheet or film causes the polymer to become substantially transparent in the area subjected to pressure or heat. These properties, however, are not common to either ethylene or propylene polymers.
- The polybutene-1 useful in this invention has a melt index between 0.1 and 25, as determined by the America Society of Testing Materials procedure ASTM D-1238T. The polybutene-1 is also substantially isotactic and is over 80 percent insoluble in diethyl ether. The polymer is preferably formed into a film or sheet by extrusion, but calendering or other methods well known in the art may be used. The thickness of the extruded or calendered product may vary from 0.5—35 mils. After forming, the polymer is aged at least three days and preferably four to eight days before stretching to develop opacity. This is approximately the time required for conversion of the Form II metastable crystalline state of polybutene-1 (which is the form obtained on cooling from the melt) to the stable crystalline Form I. Isotactic polybutene-1 is unique among the polyolefins in that it exists in at least three polymorphic forms. Upon quenching the polymer from the melt, a crystalline form of the polymer, commonly referred to as Form II polybutene-1 is obtained. Form II polybutene is well

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- characterized by its IR spectra, DTA curves, and specific volume-temperature relationship, and other parameters, and has been described as a tetragonal crystalline form. At room temperature, Form II polybutene spontaneously converts to a stable crystalline form referred to as Form I polybutene-1. The rate of conversion of Form II polymer to Form I varies with the molecular weight and purity of the polymer, as measured by the ash content. The conversion is usually essentially complete after four to seven days at room temperature. The application of stress or pressure to Form II polybutene also results in its conversion to Form I polymer. Form I polybutene-1 has been described as a rhombic crystalline form, and is well characterized by its distinctive infrared spectrum, density, DTA curve, mechanical properties, and the like. Although we do not wish to be limited by any theory of the invention, it is believed that the development of opacity upon stretching is a characteristic of the polybutene-1 in the Form I crystalline state and does not occur with polybutene-1 in the Form II or metastable crystalline state.
- The degree of opacity developed in the film on stretching increases as the degree and rate of stretching is increased. The percentage elongation of a film, after the stretching operation is completed, should be a least 50 percent, and preferably 150 to 350 percent, although a range of elongation from 50 percent to 250 percent is contemplated. The opacity obtained in the film is dependent on the rate at which stretching takes place. Maximum opacity occurs at high stretching rates, i.e., stretching rates up to and greater than 2,500 percent/min. At low rates of strain, e.g., 10 percent/min., no decrease in light transmission of the film occurs, and only moderate decreases in light transmission occur at stretching rates between 100 and 500 percent/min. The rates of stretching, however, may vary from at least 100 up to greater than 2,500 percent/min.
- Application of pressure to the nearly opaque film causes the film to become transparent to translucent, whereby the film has about the same light transmission characteristics as the original unstretched film. The minimum pressure required to cause this transformation varies from 750—800 psi, but pressures varying from 750 up to and over 1,500 psi are suitable in addition to pressures up to 20,000 psi, especially 10,000 psi and notably 1,000—1,500 psi.
- The opaque film also becomes transparent when subjected to heat. Opacity disappears at a temperature of approximately 87°C, but the transformation is substantially complete at 92°C. This temperature range is approximately 30°C below the crystalline melting point of Form I polybutene-1. It is preferred to use temperatures above 90°C, but less than 100°C to prevent distortion of the film; thus, the preferred temperature range for converting the film to a substantially transparent state is from 87°C to 100°C.
- It is a particular advantage that the clarification temperature of the opaque polybutene-1 film ranges from 87°C to 100°C, since this permits use of the opaque film in heat copying machines. The high clarification temperatures also lessen the chance of undesired development or complete clarification of the opaque film at ambient temperature, and, in this respect, is very much like the chemically treated heat copy papers presently available; however, no chemical treatment of the polymer is required.
- Small quantities of dyes or pigments can be incorporated in the film which, when stretched, provide an opaque material having a light colour. Application of pressure to the film then causes the colour of the dye or pigment to appear in those areas made transparent by the application of pressure. The quantity of dye or pigment should be 1 percent or less by weight of the polymer, and preferably between 0.01 and 0.5 percent, however, greater or lesser amounts may be used.
- Suitable dyes and pigments include: paratoner red, quinacridone red, benzidine yellow, phthalocyanine blue, phthalocyanine green, carbon black, bone black, nickel-azo-yellow, alizarin maroon, thioindigoid, indanthrone blue, and Helio-Bordeaux maroon.
- The stretched opaque polybutene-1, film may also be laminated to a coloured or non-coloured substrate, such that, after application of pressure to the laminate, the colour or background of the substrate appears through the transparent areas of the polybutene member of the laminate. Suitable adhesives for carrying out laminations to a variety of substrates, such as metal foils, coloured paper, coloured plastic films wood and ceramics, include: silicones; SR-585 silicon, manufactured by the General Electric Company; Shawinigan D-276 (Shawinigan is a Registered Trade Mark), a vinyl acetate copolymer latex manufactured by the Shawinigan Division of Monsanto Chemical Corporation; an acrylic copolymer latex; natural and nitrile rubber formulations incorporating tackifiers; Vistanex types based on polyisobutylene; and formulations of various resins, such as ethylene-vinyl acetate copolymers and polybutene-1, formulated with tackifying plasticizers.
- The above adhesives may also be coated on one surface of an opaque film or laminate made in accordance with the process of this invention and covered with a release backing. These films may be used as labels, decorative surfaces or protective surfaces.
- The following examples are given to illustrate the invention.

EXAMPLE I

Film, 7.0 mm thick, is extruded from polybutene-1 having a melt index of 0.6, as determined by the America Society of Testing Materials procedure ASTM D-1238T, and 88 percent diethyl ether insolubility. The film is allowed to age 8 days at room temperature. Strips, 1 inch wide and 4 inches long, are cut from the film. A number of the strips are stretched rapidly (at about

10,000%/minute) to 9 inches in length, whereby they become white and opaque. Eight-hundred psi pressure is applied to a number of the stretched opaque strips by means of a piston having an area of 1 square inch. The various strips are then examined in a Coleman Spectrophotometer for light transmission characteristics. The results are recorded in Table I.

20

TABLE I

	Wave Length m _u	Unstretched	% Transmission	
			Stretched	Stretched + Pressed
25	400	59	5.1	46
	450	62.5	4.3	48
	500	64.2	5.7	50
	550	67.0	6.9	51
	600	71	5.0	56
	650	72	8.3	59

30 The above data illustrate that stretching will opacify extruded and aged polybutene-1 film which may be subsequently clarified by the application of pressure.

35 **EXAMPLES II—V**
Strips of polybutene-1 film, prepared as in Example I, are mounted in an Instron (Registered Trade Mark) tensile tester, using 2 inches jaw separation and are strained to three times their original length at various rates. The light transmission characteristics of strips elongated at different rates are assessed with a Coleman Spectrophotometer. The results are listed in Table II.

45	Strain Rate (in/min.)	% Transmission	
		at 550 m _u	at 550 m _u
	2	65	
	10	54	
	20	44	
	50	14	

50 It can be seen from the above Table that opacity of the film increases rapidly at higher strain rates.

EXAMPLE VI

55 A strip of polybutene-1, extruded as in Example I, and aged six days, is rapidly stretched (at about 10,000%/minute) to 2.25 times its original length. The strip is then slit to 3/8 inch width and inserted into a printing machine comprising raised type means and a planar surface, between which the film is inserted. Sufficient pressure is applied to print on the film without distorting the tape. The stretched polybutene-1 prints well, providing sharply defined, substantially transparent, clear letters on a white, nearly opaque background. The film is also written on and provides clear images.

EXAMPLE VII

A strip of stretched, white polybutene-1 film prepared as in Example I is laminated to copper foil using Shawinigan D-267 adhesive, a vinyl acetate copolymer latex. The rear surface of the foil is also coated with adhesive and subsequently covered with silicone-treated release paper. The laminate is slit to 3/8 inch width and loaded into a printing device, as described in Example VI. Upon printing, the metallic copper colour appears as sharply defined letters and figures which contrast nicely to the white, substantially opaque background of the polybutene-1. The release paper can then be stripped from the copper foil, and the printed laminate applied to various surfaces as a label.

EXAMPLE VIII

100 parts of polybutene-1, having a melt index of 1.0, as measured by the American Society for Testing Materials procedure ASTM D-1238T, and 92 percent diethyl ether insolubility is mixed with 0.05 parts of phthalocyanine blue in a rubber mill at 240° F. The deep blue compound is extruded at 340°F, using a flat film die to provide a film 8.0 mils thick and 4 1/2 inches wide. The deep blue, transparent film is allowed to age eight days at room temperature. Strips of the film are then stretched rapidly (at about 10,000%/minute) to 2.25 times their original length, whereupon the film becomes very light blue and opaque. Strips of the stretched film are inserted in the printing device described in Example VII and printed. The strips, when printed, provide deep blue, transparent letters and figures, contrasted with an opaque, light blue background.

105 **EXAMPLE IX**
A sheet of stretched, white, opaque poly-

- butene-1 prepared as in Example 1 is held tightly against a white sheet of paper bearing black printed letters and figures. The surface of the polybutene is then exposed to an infrared lamp. After heating 1—2 minutes, an image of the printed areas appears in the polybutene-1 film as clear areas contrasted against a white background, due to the greater rate of heat absorption of the black printed figures. 5 55
- Thus, there has been described a method for opacifying polybutene-1 polymers by rapid stretching. The opaque polymer can subsequently be clarified by the application of heat or pressure. This invention has utility in the printing arts, since the opaque film may be selectively clarified by heat printing means or mechanical impact printing means. Various laminates, labels and/or pigmented compositions also may be made from the opaque polymer of this invention. 10 60
- Other uses for the opaque sheet or film of this invention include preparing various labels, decorative films and laminates, stencils for photocopying, heat-sensitive film, and the like. 15 65
- The opaque compositions of this invention may optionally include antioxidants, lubricants, extrusion aids and stabilizers in addition to colourants. 20 70
- 25 75
- 30 80
- WHAT WE CLAIM IS:—**
1. A method of opacifying a film of isotactic polybutene-1 which comprises stretching said film, to a percentage elongation of at least 50% at a rate of least 100%/min. 35 85
 2. A method according to Claim 1 wherein the elongation is from 150 to 350%. 35 90
 3. A method according to Claim 1 or Claim 2 wherein the rate of stretching is from 100 to 2,500%/min. 40 95
 4. A method according to any of the preceding claims wherein said polybutene-1 is over 80% insoluble in diethyl ether and has a melt index of from 0.1 to 25. 45 100
 5. A method according to any of the preceding claims wherein the film has a thickness of from 0.5 to 35 mils. 50 100
 6. A method according to any of the preceding claims wherein said film is formed from Form II metastable, crystalline polybutene which is subsequently converted to Form I stable crystalline polybutene-1. 50 100
 7. A method according to Claim 6 wherein said conversion is effected by aging for from 3 to 8 days.

8. A method according to any of the preceding claims wherein the film contains a dye or pigment in an amount not exceeding 1% by weight of the polymer. 55

9. A method according to Claim 8 wherein the amount is from 0.01 to 0.5%. 60

10. A method of opacifying a film of isotactic polybutene-1 substantially as described with reference to Examples I to V. 65

11. An opaque polybutene-1 film prepared by the method of any of the preceding claims. 70

12. An opaque polybutene-1 film prepared by the method of any of Claims 1 to 10 laminated to a substrate by an adhesive. 75

13. A film according to Claim 12 in which the adhesive is a silicone, acrylic copolymer latex, vinyl acetate copolymer latex, natural rubber, nitrile rubber, polyisobutylene, ethylene-vinyl acetate copolymer or polybutene-1. 80

14. A film according to Claim 12 or Claim 13 containing a release agent interposed between said substrate and said adhesive. 85

15. A method of clarifying an opaque polybutene-1 film prepared by the method of any of Claims 1 to 10 which comprises applying pressure to it in excess of 750 psi. 90

16. A method according to Claim 15 wherein the pressure is from 1000 to 1500 psi. 90

17. A method of clarifying an opaque polybutene-1 film substantially as described with reference to Examples VI to VIII. 95

18. A method of clarifying an opaque polybutene-1 film prepared by the method of any of Claims 1 to 10 which comprises applying heat to it. 95

19. A method according to Claim 18 wherein the temperature is approximately 30°C below the crystalline melting point of Form I polybutene-1. 95

20. A method according to Claim 19 wherein the temperature is from 87°C to 100°C. 95

21. A method of clarifying an opaque polybutene-1 film substantially as described with reference to Example IX. 100

22. A method according to any of Claims 15 to 22 applied to the film of any of Claims 11 to 14. 100

23. A clarified film prepared by the method of any of Claims 15 to 22.

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